NCL 70-27

STUDY OF DOPANTS FOR RADIATION-RESISTANT SILICON

QUARTERLY REPORT

APRIL 1970

Letter Contract No. 952523

NORTHROP CORPORATE LABORATORIES

3401 West Broadway
Hawthorne, California 90250

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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100

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NOTICE

This report contains information prepared by Northrop Corporate Laboratories under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or the National Aeronautics and Space Administration.

NEW TECHNOLOGY

All technological developments to date are reported herein. They are considered to be unreportable under the instructions of NHB 2170.2 dated October 1966.

ABSTRACT

Lifetime degradiation produced by Co^{60} gamma radiation was investigated in bulk silicon containing aluminum or lithium dopants. These investigations were performed to determine whether material containing these impurities is more resistant to radiation than is material which contains the more conventional dopants boron and phosphorus.

All of the Al- and Li-doped materials which were investigated proved to be more sensitive to this type of radiation than did some comparable B-doped materials investigated previously. The sensitivity of Al-doped material was found to vary from crystal to crystal but no apparent dependence on the initial resistivity or lifetime was observed.

The Li-doped samples employed in the investigation were prepared by diffusing lithium into bulk samples of P-doped material having an initial resistivity of ~ 130 ohm cm. The lithium diffused samples were approximately twenty-times more radiation resistant than comparable samples which contained other donor impurities and were more than twice as resistant as samples prepared from the undiffused material.

Annealing of crucible-grown Al-doped samples for 8 hours at $460^{\circ}C$ produced various effects. The resistivity of most of the samples increased but possible lifetime changes were obscured by severe trapping effects which were present both before and after the anneal.

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INTRODUCTION

This report describes experimental results obtained in an investigation of the effects of Co^{60} gamma radiation on minority carrier lifetime degradation in bulk silicon containing aluminum or lithium dopants. Interest in these materials was prompted by the results of earlier independent studies which indicated that, under some conditions, they or devices constructed from them are resistant to radiation. The object of the present investigation is to evaluate the recombination properties and radiation sensitivity of bulk material containing these impurities to determine whether the defects responsible for lifetime degradation involve the impurities.

TECHNICAL DISCUSSION

LIFETIME DEGRADATION STUDIES

Lifetime degradation data were presented in the last quarterly report for twenty-one samples which had been irradiated with Co^{60} gamma rays.[1] These data indicated that certain samples containing aluminum or lithium dopants are even more sensitive to this type of radiation than are samples doped with boron. These results agree with those obtained in some previous studies of similar materials but contradict the results of yet other studies.[2-7] In order to resolve this apparent contradiction and to provide a larger statistical basis for evaluating the radiation and annealing responses of these materials, additional samples containing these dopants were prepared and irradiated during the present reporting period. The experimental procedures and the total exposure dose (6.80×10^6 R) were similar to those employed in the previous irradiation. Briefly, seventeen samples were irradiated simultaneously in the Northrop Co^{60} gamma facility (dose rate 1.36×10^5 R/Hr) for a period of 50 hours. To minimize annealing during the relatively long exposure period, the samples were packed in dry ice (195°).

The experimental results are summarized in Table I which lists the initial and post-irradiation lifetimes of each sample at 30°C and the calculated lifetime damage constant. For our purposes, we define the damage constant, K, through the relationship

$$\frac{1}{\tau_{\phi}} = \frac{1}{\tau_o} + \frac{\phi}{K}$$

TABLE I - Lifetime Damage Constants for Silicon Samples Irradiated with 1.1×10^{16} Co^{60} Gammas/cm^2

Sample	τ_o μs	τ_ϕ μs	K γ's/cm^2 $\mu s \times 10^{17}$
DCB 11.6	11.0	7.9	3.14
GCA1 6.3	17.3	7.2	1.36
GFA1 4.2	60.6	8.2	1.05
GFA1 9.4	310	12.2	1.40
GFA1 10.0	382	11.9	1.35
GFA1 9.9	164	25.2	3.28
GFA1 10.0	170	26.4	3.44
GFA1 10.1	167	25.1	3.25
GFA1 10.2	173	25.1	3.23
TLA1 6.1	115	8.4	0.99
TLA1 6.4	115	8.2	0.97
TLP 126*	96.7	2.7	0.30
TLP 130	136	2.8	0.31
TLP(Li) 1.0**	144	6.5	0.74
TLP(Li) 3.9*	222	4.7	0.52
TLP(Li) 5.1*	188	5.4	0.61
TLP(Li) 6.2*	162	7.9	0.92

* Annealed 12 hours at 400°C in vacuum

** Annealed 24 hours at 425°C in vacuum

where τ_o and τ_ϕ are the initial and post-irradiation lifetimes at 30°C and ϕ is the gamma dose. Defined in this manner, K, represents the gamma dose required to reduce the lifetime of an initially perfect sample ($\tau_o \simeq \infty$) to 1μs and is thus indicative of the radiation "hardness" of the material. Note however, that the damage constant defined by the above relationship is the reciprocal of that sometimes used in radiation effects studies.

The sample designation employed in the table denotes the crystal manufacturer, growth method and dopant and the measured room temperature resistivity of the sample, respectively. Manufacturers D, G, and T are the Dow Corning Corporation, General Electric Company, and Texas Instruments, Inc. respectively. Growth method "C" is the Czochralski or pulled (quartz crucible) technique and is expected to produce crystals having relatively high oxygen concentrations ($> 10^{17}$ cm^{-3}). In contrast, growth methods "F" (float-zone in argon ambient) and "L" (Lopex) are expected to produce "oxygen-free" material ($\lesssim 3 \times 10^{16}$ cm^{-3}).

The last four samples listed in the table were prepared by diffusing lithium from a lithium-aluminum hydride source into ~ 7 x 7 x 30 mm blanks made of ~130 ohm cm phosphorus-doped silicon which was grown by the Lopex process (i.e. TLP 130 material). Samples were immersed in a 4.2 molar solution of the hydride in ether and allowed to air dry. They were then heated for 5 to 10 minutes in vacuum at 400° or 425°C to diffuse the lithium. Following this treatment, they were quickly cooled to room temperature and were both lapped and etched to remove any excess lithium remaining on or near the surface. They were then reheated in vacuum for 12 to 24 hours at the previously employed diffusion temperature to distribute the diffused lithium more uniformly through the samples.

Results of previous studies and measurements of the resistivity profile of each sample indicated that these treatments were successful.

To determine what effects the heat treatments alone might have on this material, sample TLP 126, which did not contain lithium, was annealed for 12 hours at 400°C with samples TLP (Li) 5.1 and TLP (Li) 6.2. The two latter samples contained lithium previously introduced during a 5 minute diffusion at this temperature. Lifetime and resistivity measurements performed on the samples before and after the 12 hour anneal revealed that neither of these properties was altered appreciably in the undiffused sample. Interestingly, at room temperature and above the lifetimes of the diffused samples were also relatively unaltered by the introduction and distribution of lithium. In contrast, the resistivity of the material was reduced by more than a factor of 20. However the diffused samples did exhibit trapping effects below room temperature, which were not observed in the undiffused sample. These effects are apparently due to trapping centers associated with defects involving lithium and become effective only below room temperature.

For ease of comparison, samples which were prepared from the same crystal are grouped together in Table I. An examination of the data reveals that the damage constants of identical samples are very consistent but the magnitude of the constant for Al-doped material varies strongly from crystal to crystal. Variations of this sort have been observed in this material previously and are apparently unrelated to the initial resistivity (dopant concentration) or the initial lifetime of the sample.[1, 2] On the other hand, the resistivity and the lifetime of both Al and Li-doped materials have been found to be extremely sensitive to pre-irradiation heat treatments.[1] Consequently, the difference in the damage constants

of Al-doped samples from different crystals but which are identical in other respects may be due to small differences in the crystal growth techniques. These growth differences may produce different defect concentrations or distributions in the crystals.[8,9] The effect of such differences is illustrated in Figure 1 which shows the temperature dependence of the lifetime for three Al-doped samples prepared from different crystals. Observe the relatively large difference in both the shapes and the positions of the curves for samples GFAl 9.4 and GFAl 10.1. As indicated by their designations, these samples were essentially identical. The temperature dependences exhibited by samples TLAl 6.4 and GFAl 9.4 are more similar even though these samples differ in most other respects (manufacturer, growth method, etc.).

With the exception of the four GFAl samples which were prepared from the same crystal, the damage constants of all of the Al-doped samples indicated in Table I are significantly smaller than those exhibited by comparable B-doped samples in previous studies. This behavior agrees with that reported in the last report and confirms that some Al-doped silicon is more sensitive to Co^{60} gamma radiation than is comparable B-doped material.

Data for only two crucible-grown samples (DCB 11.6 and GCAl 6.3) are included in the table. Samples from these and other Czochralski crystals exhibited severe trapping effects which prevented accurate lifetime determinations using the photoconductivity decay technique. However, it may be possible to investigate more of these materials in the future by using a scanning electron microscope to measure the diffusion lengths and consequently the lifetimes. This technique is in the development stage but should provide accurate lifetime values regardless of the amount or type of trapping present. An additional DCB sample was irradiated but the post-irradiation lifetime of the sample and, consequently, the damage constant

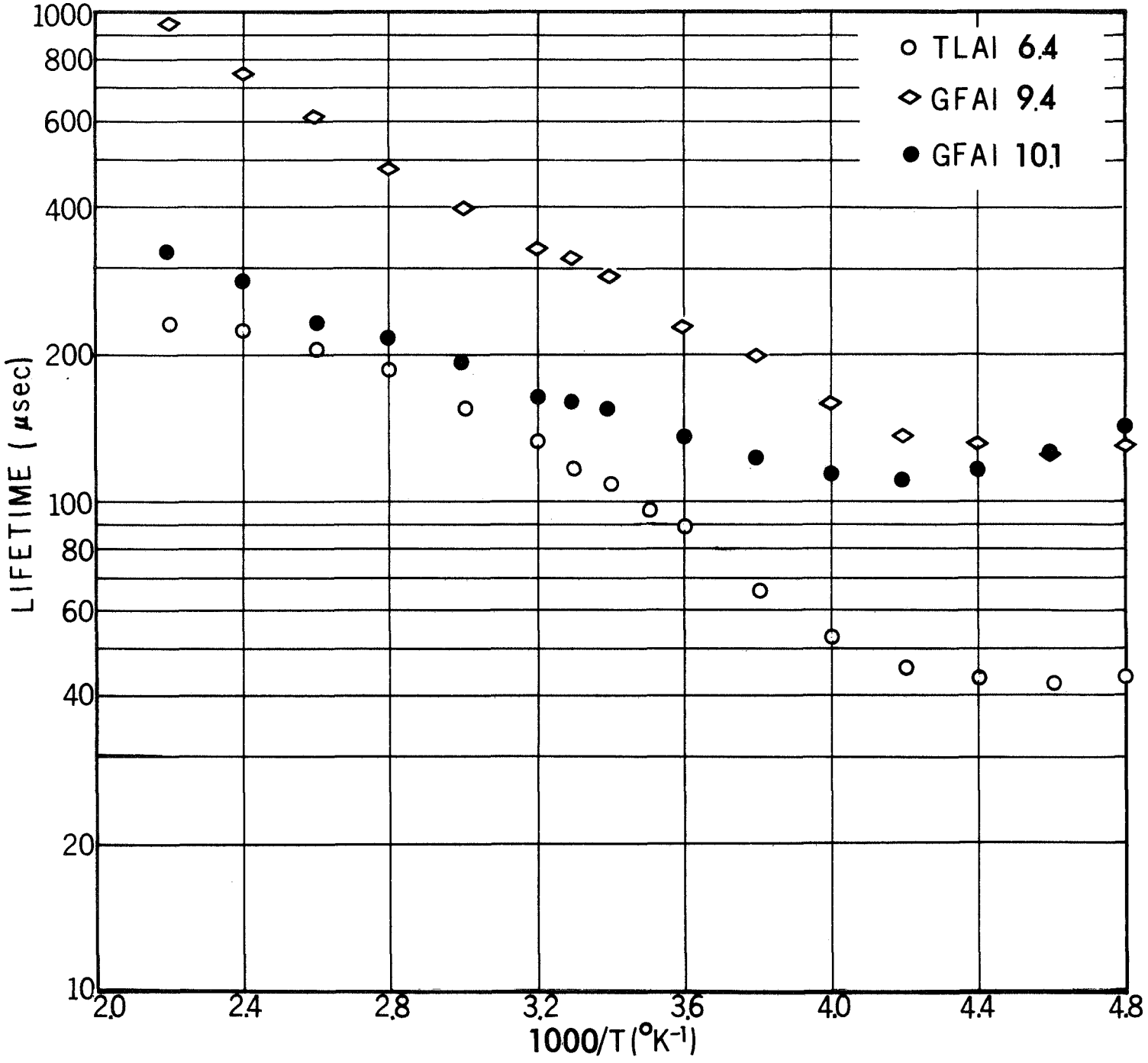

Figure 1. Temperature Dependence of Lifetime of Samples from Three Al-doped Crystals

could not be determined accurately due to extremely large trapping effects. However, results of previous studies of crucible-grown samples indicate that lifetime degradation in p-type material by Co^{60} gamma radiation is not greatly influenced by the oxygen concentration alone.[1,2]

The two TLP samples listed in the table did not contain lithium and were irradiated to provide a basis for evaluating the effect of lithium on the radiation response of this material. As mentioned above and as noted in the table, sample TLP 126 was heat treated before the irradiation. The fact that the damage constants obtained for these samples are essentially identical indicates that this treatment did not affect the sensitivity of this material to radiation. The temperature dependence of the pre-irradiation lifetimes of these samples is illustrated in Figure 2 and the fact that the shapes of the curves are similar is further evidence that the heat treatment did not alter the recombination properties of the sample. The data shown in the figure were obtained by measuring the lifetimes of the samples at selected temperatures as they were heated slowly from 30°C to 203°C ($1000/T = 2.1K^{-1}$). The samples were then cooled slowly to the lowest temperature and warmed back to 30°C for final lifetime measurements. During both the heating and cooling cycles, measurements were performed at alternate temperatures to determine whether the data were reproducible. The arrows attached to some of the data points of sample TLP 126 indicate that the lifetime of this sample decreased after it was heated. Similar behavior has been observed in samples from both this and other crystals having long lifetimes, however. This behavior is attributed to surface states introduced by heating since the lifetimes are reproducible at lower temperatures. Consequently, the apparent lifetime reduction exhibited by sample TLP 126 is probably not related to the previous anneal of the sample.

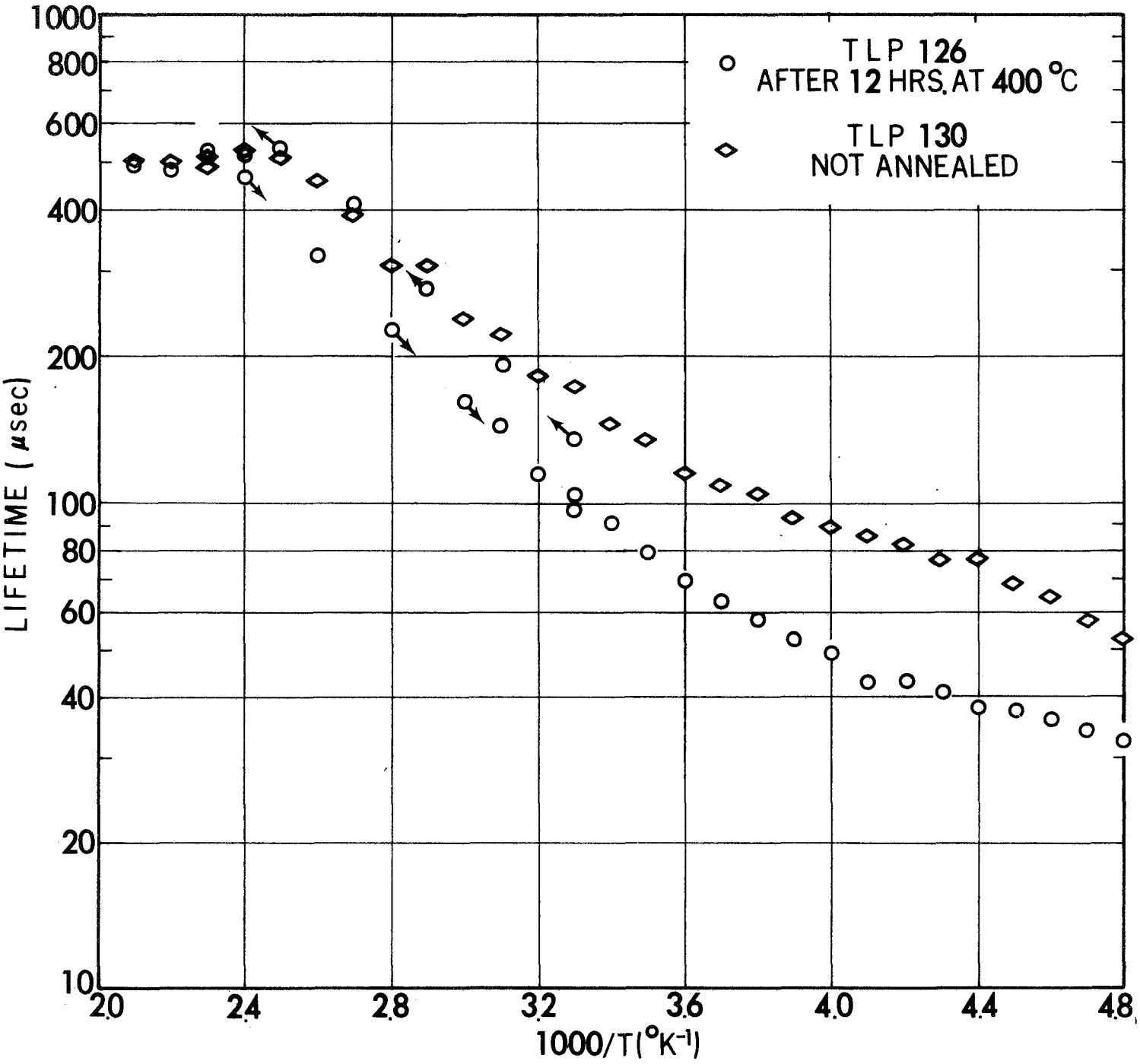

Figure 2. Temperature Dependence of Lifetime of TLP 130 Material before Irradiation

The Li-doped samples indicated in Table I exhibit a relatively large range of damage constants. However, in contrast to the results presented in the last report, the damage constant does not appear to be related in the normal way to the sample resistivity.[1] Although all of these samples were more radiation sensitive than comparable p-type samples which contained either aluminum or boron dopants, they were less sensitive than the TLP material from which they were made. Even more significant is the fact that they are approximately twenty times more resistant than 10 ohm cm P-doped float-zone samples which were irradiated in a previous study.[2]

ANNEALING OF UNIRRADIATED Al-DOPED SAMPLES

Eleven Al-doped crucible-grown samples which had initial lifetimes shorter than $\sim 10\ \mu s$ and which exhibited excessive trapping were annealed for 8 hours at 460°C to determine the effect of this treatment on the electrical properties and subsequent radiation response of this material. In an earlier experiment, two similar samples were converted to high resistivity n-type after heating for 24 hours at this temperature.[1] However, the use of a shorter annealing period was expected to produce more moderate changes in the later samples.

Four of the heat treated samples were obtained from four different General Electric crystals which had very short lifetimes. Before they were annealed, the recombination behavior of these samples was dominated by a very slow trapping center with an effective lifetime of approximately 1 second at room temperature. The lifetime of one of the samples was measured as a function of temperature and the results are shown in Figure 3. Observe that in the range from approximately 40°C to 100°C ($2.7 \lesssim 1000/T \lesssim 3.2$), the apparent lifetime of the sample decreased by more than three orders of magnitude. This behavior and the apparent

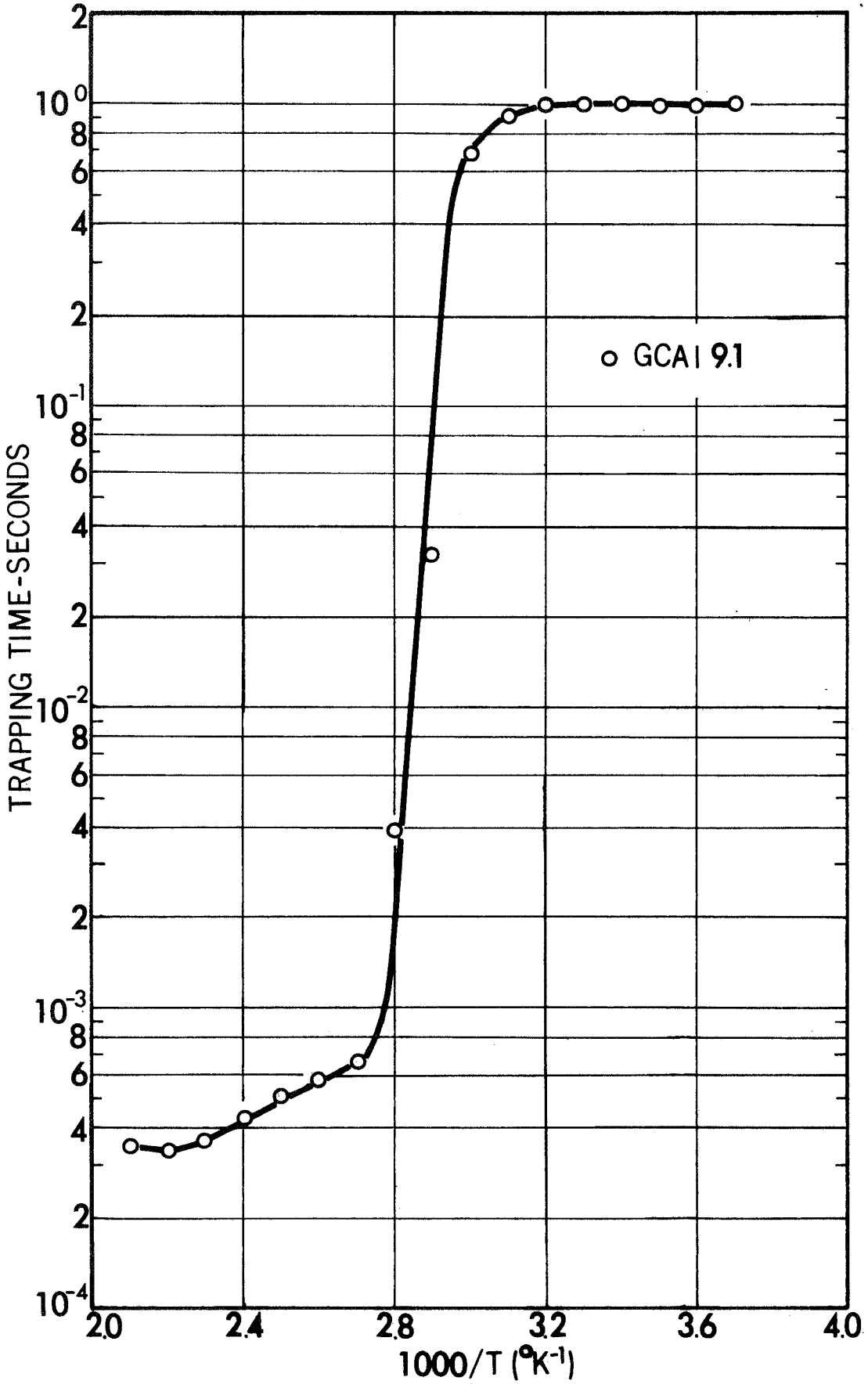

Figure 3. Recombination Behavior of an Al-doped Sample Showing the Effects of Slow Traps

decrease in lifetime with increasing temperature confirms that the photoconductivity decays were associated with trapping time constants rather than recombination processes.

Since the initial lifetimes of most of the eleven samples were uncertain because of large trapping effects, the sample resistivity was also monitored to determine the effects of the 8 hour anneal. The resistivities and lifetimes at room temperature before and after the anneal are shown in Table II. The initial resistivity values were determined from potential profiles which were performed on each sample before the anneal. The post-irradiation values were calculated from the measured resistance at room temperature. Consequently, the small resistivity changes indicated for some samples may be due to differences in the measurement techniques. The sample designation is the same as that used in Table I. Manufacturers A and E are the Allegheny Electronic Chemicals Company and the Electronic Space Products, Inc., respectively.

An examination of the data in Table II shows that the resistivity of most of the samples increased as a result of the anneal. However, the amount of increase varies widely and does not appear to be related to the initial value. Since soldered contacts were used on the samples, it was necessary to remove them before the anneal and to replace them afterward. The quality of the replaced contacts was determined by measuring the sample resistance in reverse directions at both room temperature and dry ice temperature. Such measurements will disclose rectifying contacts but will not reveal high resistance contacts which do not rectify. Consequently, it is possible that some of the indicated resistivity changes include contact effects. With the exception of samples GCA1 5.8 and GCA1 9.1, none of the samples rectified after the anneal. Additional measurements on these samples revealed that the rectification occurred at a junction in the material which was not observed before the anneal and did not involve the contacts.

TABLE II - Effect of Heating for 8 hours at 460°C on the Lifetime and Resistivity of Al-doped Silicon

Sample Designation	Crystal No.	Resistivity - ohm cm		Lifetime - μs*	
		Initial	Final	Initial	Final
GCAl 4.0	CZ 88	4.0	333	(T)	65 (T)
GCAl 4.0	CZ 82	4.0	20	(T)	15 (T)
GCAl 5.8	CZ 87	5.8	75-265	(T)	(R)
GCAl 9.1	CZ 84	9.1	94-361	(T)	(R)
ACAl 1.8	6170-1	1.8	2.96	<1.0(T)	(T)
ACAl 1.8	6170-1	1.8	1.93	<1.0	(T)
ACAl 3.7	6170-3	3.7	8.6	14.3(T)	11 (T)
ACAl 4.9	6170-3	4.9	5.3	<1.0(T)	1.6
ACAl 5.0	6170-3	5.0	4.9	8.7(T)	8.1 (T)
ECAl 1.5	202	1.5	4.2	<1.0(T)	(T)
ECAl 1.7	202	1.7	177	<1.0(T)	(T)

*Lifetime value uncertain due to rectification (R) or trapping (T).

As indicated in the table, no significant improvement in the lifetime of any of the samples was observed after the anneal. However, all of the samples continued to exhibit excessive trapping effects which made the lifetime measurements extremely difficult. It is consequently possible that these effects obscured any lifetime increases in the samples. Such increases were particularly possible in samples GCAl 4.0 (crystal CZ 82) and ECAl 1.5 which exhibit significant but reasonable resistivity changes. The two GCAl samples which rectified displayed particularly strange behavior due to the presence of the junction in them. The photoconductivity decay curves of these samples were extremely non-exponential and the polarity of the signal could be reversed by reversing the samples in the holder used for these measurements.

CONCLUSIONS

The results of the present study of lifetime degradation in Co^{60} gamma-irradiated silicon agree with those obtained previously. They indicate that certain materials which contain aluminum or lithium dopants are more sensitive to this type of radiation than are B-doped materials. On the other hand, samples which contain lithium are approximately twenty times more resistant to radiation than are comparable samples which contain other donor impurities. Low resistivity samples prepared by diffusing lithium into high resistivity P-doped material are also more radiation resistant than samples prepared from the undiffused material.

Attempts to improve the lifetimes of Al-doped samples by annealing for 8 hours at $460^{o}C$ were not successful. This treatment did cause an increase in the resistivity of most of the samples indicating that the type, concentration, and/or distribution of defects or donors was altered. Unfortunately, these changes did not affect the recombination properties of this material.

FUTURE PLANS

Some of the previously irradiated samples will be isochronally annealed during the next reporting period to study lifetime recovery in the various materials. In the performance of these studies, lifetime measurements will be performed as a function of temperature for samples containing different dopants to determine whether the radiation induced recombination centers involve dopant impurities.

The diffusion lengths of samples GCA1 4.0 (crystal CZ 82) and ECA1 1.5 of Table II will be measured using the scanning electron microscope technique. If these measurements reveal that the lifetimes of the samples are greater than $\sim$15 μs, the samples will be irradiated and the measurements will be repeated to determine the effect of the previous heat treatment on the radiation response of these materials.

REFERENCES

1. Second Quarterly Report "Study of Dopants for Radiation-Resistant Silicon," NCL 70-1R, January 1970.

2. R. F. Bass and O. L. Curtis, Jr., "Effects of Impurities on Carrier Lifetime in Bulk Solar-Cell Material," Northrop Corporate Laboratories, Report 69-29R, May 1969.

3. O. L. Curtis, Jr., R. F. Bass, and C. A. Germano, "Radiation Effects in Silicon and Germanium," Harry Diamond Laboratories, Washington, D. C., Report 235-2, November 1966.

4. O. L. Curtis, Jr., R. F. Bass, and C. A. Germano, "Radiation Effects in Silicon and Germanium," Harry Diamond Laboratories, Washington, D. C., Report 235-3, November 1967.

5. O. L. Curtis, Jr., J. R. Srour, R. F. Bass, and E. G. Wikner, "Radiation Effects in Silicon and Germanium," Harry Diamond Laboratories, Washington, D. C., Report 235-5 to be published.

6. V. S. Vavilov in Radiation Damage in Semiconductors, Academic Press, New York (1964) p 115

7. J. J. Wysocki, IEEE Trans. Nuc. Sci. NS-13, 6, 168 (1966).

8. C. S. Fuller and R. A. Logan, J. Appl. Phys. 28, 1427 (1957).

9. C. S. Fuller, F. H. Doleiden, and Katherine Wolfstirn, J. Phys. Chem. Solids, 13, 187 (1960).